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THIN FILM SOLID LUBRICANT DEVELOPMENT

FINAL REPORT

Submitted by:

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A cooperative agreement, between St. Louis University and the NASA Lewis Materials Division, was entered into in order to develop effective tribological coatings for high temperature sliding applications. During the initial phase of the agreement, the tribological limits of an Au/Cr coating on alumina substrates in sliding at high temperature were quantified^{1,2,3}. Alumina test disks were sputter coated with the Au/Cr solid lubricant and subsequently tribo-tested in the NASA Lewis high temperature pin on disk tribometer. An appropriate test matrix was developed in cooperation with Dr. C. DellaCorte of NASA Lewis. The test program was designed to determine the load, speed and temperature extremes that the Au/Cr solid lubricant coating could endure. Surface profilometry data of disk wear tracks was performed at Lewis and then the disks and pins were sent to St. Louis University for SEM/EDS analysis, data reduction and synthesis.

Friction was reduced by 30 to 50% at all temperatures tested up to and including 1000°C, when compared to unlubricated baseline sliding of alumina vs. alumina. Similar reductions in friction were observed as load was increased from 4.9 to 49 N. Wear factors were reduced by 1 to 2 orders of magnitude under all temperature and loading conditions. Localized coating penetration occurred at loads above 7.4 N in central regions of the wear track. However, enough of the coating remained to carry the load without significant increase in either pin wear factor or friction coefficient. As might be expected increasing the sliding speed led to earlier wear through of the solid lubricant film. Friction coefficient was not significantly effected by increase in sliding velocity.

Based on its superb performance during the preliminary pin-on-disk testing the Au/Cr coating was investigated as a possible solid lubricant for high temperature foil-bearing applications, turbo-chargers, etc. During normal steady state operating conditions contact between the journal and the mating foil in this type of bearing is non-existent: The journal rides on a film of air. However, during start-up and shut-down operations the air film dissipates and a full contact, severe wear condition develops. A protective coating on either the foil and/or the journal is therefore required to prevent wear during the normal start-stop events experienced over the lifetime the bearing.

A preliminary investigation involved wear testing of foils coated with the Au/Cr high temperature solid lubricant. Foils made of super-alloy INX-750 were coated with Al_2O_3 , then top-coated with Au/Cr. The coated foils were then tested in the NASA Lewis high temperature half bearing test rig. The NASA half bearing test rig reproduces the severe contact regime encountered during start-up and shut-down operations involving foil bearings. Journal and foil wear surfaces underwent SEM/EDS post-test analysis at SLU. Extensive wear-through of the coated foils was observed after 5,000-15,000 start stop cycles at both room temperature and 500°C.

Therefore the research direction was modified to include coating of the journals as well as the foils with a high temperature solid lubricant. However, cost considerations precluded coating the journals with the Au/Cr solid lubricant. Instead they were coated with the new PS30X series of solid lubricants. This series, the latest in the NASA developed PSXXX solid lubricants, is a chrome oxide, nichrome based plasma spray coating, with fluorides (BaF_2 and CaF_2) added for high temperature lubrication, and silver for low temperature lubrication. The coated journals were wear tested in the NASA half bearing test rig for up to 15,000 start-stop cycles against uncoated INX750 foils as well as

foils coated with Al_2O_3 . SEM/EDS analysis at SLU showed minimal wear of both journals and foils whether the foils were coated or not.

This co-operative agreement has led to the publication of two journal articles, one NASA Tech Memo and a soon to be published NASA Tech Brief. An additional NASA Tech Memo and subsequent journal article detailing the results of the foil bearing tests are in the process of being prepared. I believe that this co-operative venture has benefited both NASA and St. Louis University, and has ultimately expanded the knowledge base of the tribological community. It has been a pleasure to work with the NASA Lewis scientists, engineers and technicians and I hope to be able to work with them again in the future.

¹ "Au/Cr Sputter Coating for the Protection of Alumina During Sliding at High Temperatures," *Tribology Transactions*, Vol. 39, No. 3, 7/1996, pg. 670-676 with C. DellaCorte.

² Benoy, P. A., DellaCorte, C. "Au/Cr Sputter Coating for the Protection of Alumina During Sliding at High Temperatures" Poster presentation, 1994 Gordon Conference on Tribology, July 5, 1994.

³ Benoy, P. A., DellaCorte, C., "Tribological Characteristics of Sputtered Au-Cr Films on Al_2O_3 Substrates at Elevated Temperatures," *Surface Coatings and Technology*, Vol. 62, Number 1-3, December 10, 1993. Presented at the International Conference on Metallurgical Coatings and Thin Films, April 19 - 23, 1993.



Au/Cr Sputter Coating for the Protection of Alumina During Sliding at High Temperatures[©]

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A sputter-deposited bilayer coating of gold and chromium was investigated as a potential solid lubricant to protect alumina substrates in applications involving sliding at high temperatures. The lubricant was tested in a pin-on-disk tribometer with coated alumina disks sliding against uncoated alumina pins. Three test parameters—temperature, load and sliding velocity—were varied over a wide range in order to determine the performance envelope of the Au/Cr solid lubricant film. The tribo-tests were run in air at temperatures of 25° to 1000°C, under loads of 4.9 to 49.0 N and at sliding velocities from 1 to 15 ms⁻¹. Posttest analyses included surface profilometry, wear factor determination and SEM/EDS examination of worn surfaces.

Compared to unlubricated Al₂O₃ sliding, the use of the Au/Cr film reduced friction by 30 to 50 percent and wear by one to two orders of magnitude. Increases in test temperature resulted in lower friction and the Au/Cr film continued to provide low friction, about 0.3, even at 1000°C. Pin wear factors and friction were largely unaffected by increasing loads up to 29.4 N. Sliding velocity had essentially no effect on friction, however, increased velocity reduced coating life (total sliding distance). Based upon these research results, the Au/Cr film is a promising lubricant for moderately loaded, low-speed applications operating at temperatures as high as 1000°C.

KEY WORDS

Solid Lubrication, Gold, Chromium, Ceramics, High Temperatures

INTRODUCTION

Ceramics, such as alumina, with their low thermal conductivity and high temperature stability, are attractive materials for high-temperature applications (1). However, if they are to be used in sliding contacts, an appropriate lubrication scheme must be implemented. Thermal breakdown renders

typical liquid lubricants ineffective above temperatures of approximately 350°C (2). Therefore, the authors have chosen to investigate solid lubrication, using a sputter-deposited bilayer coating of Au and Cr, for the protection of alumina substrates during sliding at elevated temperature.

The use of thin soft coatings of materials such as gold to protect hard substrates is not new technology (3). While soft coatings, such as gold, lead, copper, silver and others have historically been used to protect harder substrates, using soft metallic films to protect ceramic surfaces is a rather recent development. The underlying principle remains the same whether the substrate is metallic or ceramic; under a sliding load the soft overlayer shears rather than abrades, protecting the hard substrate which in turn actually carries the load. The following simple equation, based on the junction theory of friction, models this principle and can be used to estimate the coefficient of friction for hard substrates lubricated by thin soft solid films:

$$\mu = \tau_i / p_0$$

where τ_i is the shear strength of the interfacial thin solid and p_0 is the indentation pressure of the substrate material (4).

A number of studies have been done recently utilizing thin silver films to lubricate ceramics at temperatures up to 570°C (5)–(8). In the present study, a thin gold layer was chosen as a solid lubricant because of its chemical stability and relatively high melting temperature, 1073°C. Unfortunately, because it is nonreactive, gold adheres poorly to ceramic substrates (9). The contact angle, θ , which characterizes the wettability of two substances, is 140 degrees between gold and monocrystalline alumina, indicating that gold is nonwetting on aluminum oxide (10).

This difficulty may be overcome by using a binder layer of a more reactive metal between the gold and the alumina substrate. The electronics industry typically uses a bond layer of chromium between gold electrical contacts and underlying silicon substrates (11). Although silicon lacks the mechanical strength for load bearing applications, the use of a chromium underlayer can be applied to more likely bearing substrates such as alumina. During preliminary testing described in a

previous publication, it was demonstrated that the Au/Cr material combination successfully lubricated alumina at temperatures to 800°C (12).

The current investigation was undertaken to further characterize the operating limits and performance of the Au/Cr high-temperature solid lubricating system. Au/Cr sputter-coated alumina disks were tested in a high-temperature pin-on-disk tribometer at temperatures of 25°, 250°, 500°, 800° and 1000°C under normal loads ranging from 4.9 N to 49.0 N and sliding velocities from 1 to 15 ms⁻¹. Posttest wear measurements and microscopy were used to analyze the specimens and help elucidate the wear process.

EXPERIMENTAL

Materials/Specimen Preparation

Disks and pins were made from sintered α -alumina (99.4 percent pure, physical properties delineated in Table 1), diamond-ground to achieve final dimensions. Typical as-ground surface finish was 0.1 to 0.2 μ m rms. The sputter targets of gold and chromium had purities of 99.999 and 99.95 percent, respectively.

The alumina disks were ultrasonically cleaned for 15 minutes in acetone followed by 15 minutes in methanol to remove surface contamination. Immediately prior to the coating deposition, the Al_2O_3 disks were backsputter-etched with argon to remove adsorbed surface contaminants. The disks were then RF Magnetron-sputter coated with 100 nm of Cr, and finally overcoated with 2 μ m of Au. Details of the sputtering technique have been described previously (12).

During the preliminary testing, a Cr thickness of 50 nm was used. At high temperature (800°C) this coating suffered sporadic delamination failures. Doubling the Cr layer to 100 nm eliminated the delamination failures. The 2 μ m Au coating thickness was not optimized in this study. However, Maillat et al. (7) in their investigation of silver films found that a 2 μ m thickness was optimal. Future research may be conducted to investigate film thickness effects but this is beyond the scope of the current study.

After sputter coating, the disk specimens were heat treated in air for 6 hr at 800°C. This heat treatment, modified slightly from the previous study which used an annealing temperature of 725°C, was found to produce a more tenacious coating. EDS analysis of post-heat-treated disk specimens, which appear gray-green after heating, revealed Cr diffusion into the 2 μ m Au layer, as Fig. 1 shows. Both diffusion and oxide

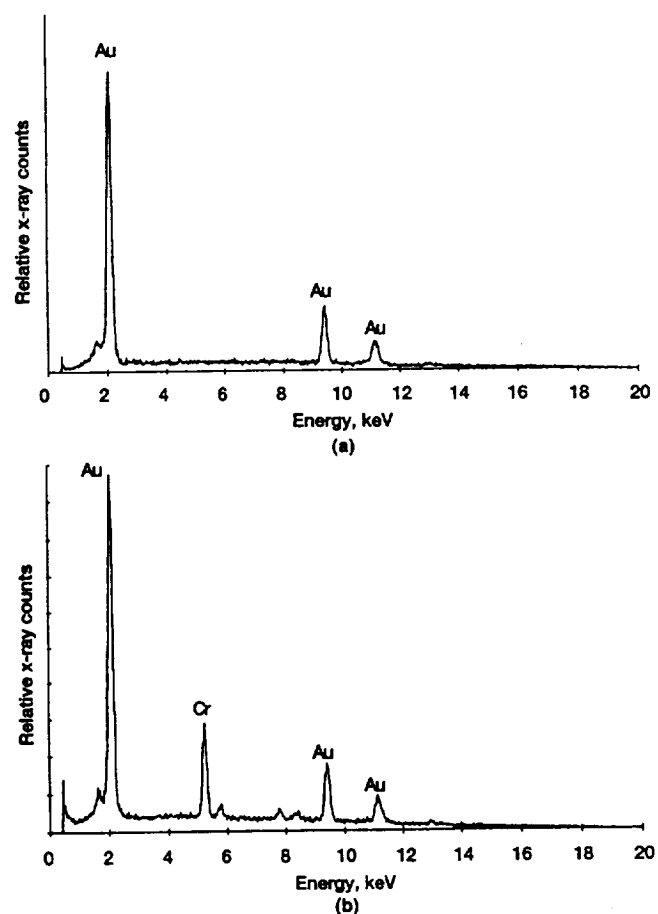


Fig. 1—EDS X-ray spectra of a 2 μ m thick AuCr film on Al_2O_3 substrate (a) as-deposited and (b) after heating in air at 800°C for six hr (electron beam energy 20 kV). Peaks at ~8 keV artifacts from sample holder.

formation may ultimately be shown to play a role in the adhesion of the coating. However, no specific efforts were made in this investigation to determine either the surface layer or substrate Al_2O_3 -Cr interface chemistry or morphology.

A 2.54 cm radius of curvature was machined on 9.55 mm diameter alumina rods to act as pins during the tribo-testing. The pin surfaces were then polished to a finish of 0.2 μ m rms. The pins were prepared for testing by rinsing with ethyl alcohol, scrubbing with levigated alumina powder and water, rinsing with deionized water, and finally drying with compressed air.

Experimental Apparatus/Method

Pin-on-disk testing was performed in a high temperature tribometer which has been extensively described and pictured in a previous publication (13). Both the pin and disk were enclosed in a resistance-heated furnace. Each alumina disk was aligned in the tribometer prior to tribo-testing to reduce total indicated run-out to less than 12.2 μ m. The pin was loaded on the rotating disk surface using dead-weights. Rotational speed was varied from 370 to 5640 rpm, corresponding to nominal tangential velocities of 1 to 15 ms⁻¹. The majority of tests were run for a period of 1 hr and at 1 ms⁻¹ sliding velocity in order to make comparisons to earlier data. Testing at higher speeds (> 1 ms⁻¹) was limited to 30-minute durations due to rapid coating wear through and

TABLE 1—PROPERTIES OF Al_2O_3 MATERIAL TESTED

PROPERTY	VALUE
Composition	99.4 wt% Al_2O_3 and trace Fe, Si
Density	3.9 g cm ⁻³
Young's modulus	386 GPa
Vickers hardness	2000 kgf mm ⁻²
Toughness	4.2 MPa m ^{-1/2}
Thermal expansion coefficient	8.0 $\times 10^{-6}$ °C ⁻¹
Four-point bend strength	344 MPa
Poisson's ratio	0.23
Thermal conductivity	22 W m ⁻¹ °C ⁻¹

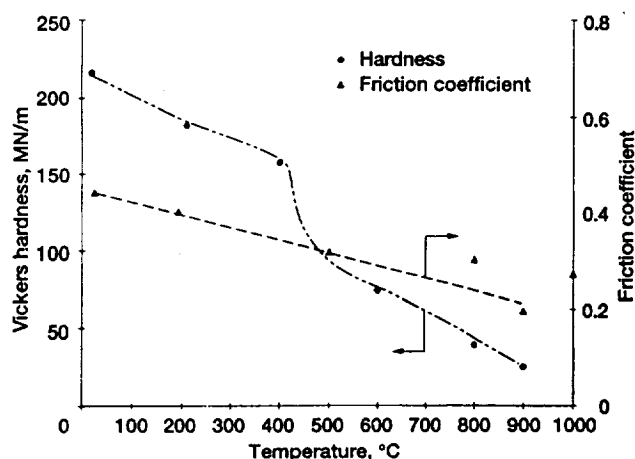


Fig. 3—Vickers hardness of gold and Au/Cr friction coefficient as a function of temperature. The hardness data is from Ref. (15).

of course, limited by the melting point of the gold lubricant layer ($\approx 1073^\circ\text{C}$). Based upon these results, it appears plausible that the test temperature is affecting friction through a shear-strength reduction mechanism. Test temperatures in excess of 1000°C were not attainable because the Al_2O_3 disk specimens repeatedly failed by fracture.

Pin wear, given in Table 2, showed no consistent trends with changing test temperature. Differences in the average pin wear factors measured at various test temperatures were generally within data scatter. For example, at a load of 4.9 N, the pin wear factor at 1000°C was $17.4 \pm 13 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ while at 25°C it was $7.0 \pm 0.8 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, indicating that although the average values differed, they were still within the scatter band of one standard deviation. The similarity of the pin wear factors may be due, in part, to the fact that compared to the alumina pin surface, the Au/Cr coating is very soft at all of the test temperatures and thus has a small effect on pin wear.

Disk wear is not reported in this study. Preliminary testing suggested that disk wear measurements for Au/Cr coated specimens may not be meaningful (12). The primary function of a thin film lubricant is to protect the substrate and reduce friction. Since the tests conducted here generally ended before the films completely wore through, all of the disk wear depths were comparable at $\approx 2 \mu\text{m}$. Therefore, direct comparison of Au/Cr-lubricated disk wear to unlubricated alumina disk wear was not made. For quantitatively characterizing the overall performance of the lubricant coating, only friction and counterface wear are considered.

Effect of Load

The effect of load on friction is given by the data in Table 2 and is illustrated graphically in Fig. 4. The data show that, within scatter, load has little or no effect on friction. At room temperature, 25°C , a tenfold increase in load, from 4.9 N to 49 N, produced only a 15 percent increase in friction coefficient, from 0.49 to 0.57. Similar behavior was observed at 800°C a fivefold increase in load, from 4.9 N to 29.4 N, resulted in a 30 percent increase in friction coefficient, from 0.30 to 0.39. At all loads, 4.9 to 49 N, the friction coefficients of coated disks remained 30 to 50 percent less than those of

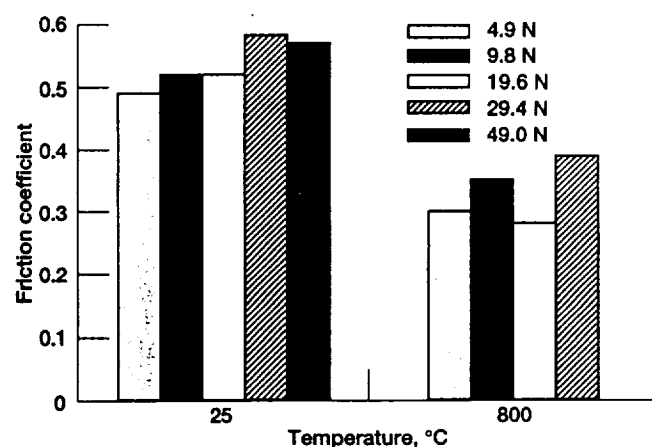


Fig. 4—Friction coefficient of Au/Cr coated alumina as a function of load at 25°C and 800°C (1 ms^{-1} sliding velocity, air atmosphere).

uncoated disks tested under a 4.9 N load. The slight increase in friction coefficient with increased load may be due to the partial penetration of the solid film at extreme loads as discussed below. Bowden and Tabor reported similar behavior for indium on steel, indium on silver, and lead on steel and copper (3).

Test load had little or no effect on pin wear at lower test load as shown in Table 2. The pin wear factors remained essentially constant as load was increased up to 19.6 N, but at higher loads, pin wear factors increased. For example, at 25°C , the pin wear factor was approximately $8 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for loads between 4.9 and 19.5 N. The wear factor increased to approximately $26 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ at 29.4 N and further increased to $47 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ at 49 N. Despite this increase, the pin wear factors produced under even the most severe load conditions (49 N) with coated disks remained an order of magnitude lower than those produced under even the mildest load conditions (4.9 N) on uncoated disks.

Increasing the load above 7.4 N resulted in partial penetration of the protective gold coating at all temperatures. Surface profilometry traces of wear tracks produced during higher load tests showed localized areas where track depth exceeded the two-micron gold coating thickness, indicating that some substrate wear occurred. As the load was increased, the coating penetration or degradation became more severe. The more extensive coating penetration observed at higher loads is a possible cause of the three and six fold increase in pin wear as load was increased to 29.4 and 49.0 N, respectively. A breach in the solid lubricant coating would result in periodic direct contact between the alumina pin and the exposed substrate which, in turn, would lead to higher pin wear.

SEM and EDS analyses were conducted on disk wear tracks after testing to identify possible wear mechanisms and to better understand the wear process. SEM photomicrographs confirm the localized coating penetration. Figures 5(a)–5(d) are electron micrographs at increasing magnifications of a wear track after sliding under a 9.8 N load. Three types of morphological regions characterized the wear track surface:

1. Large predominant regions of intact Au/Cr which provide continued lubrication.

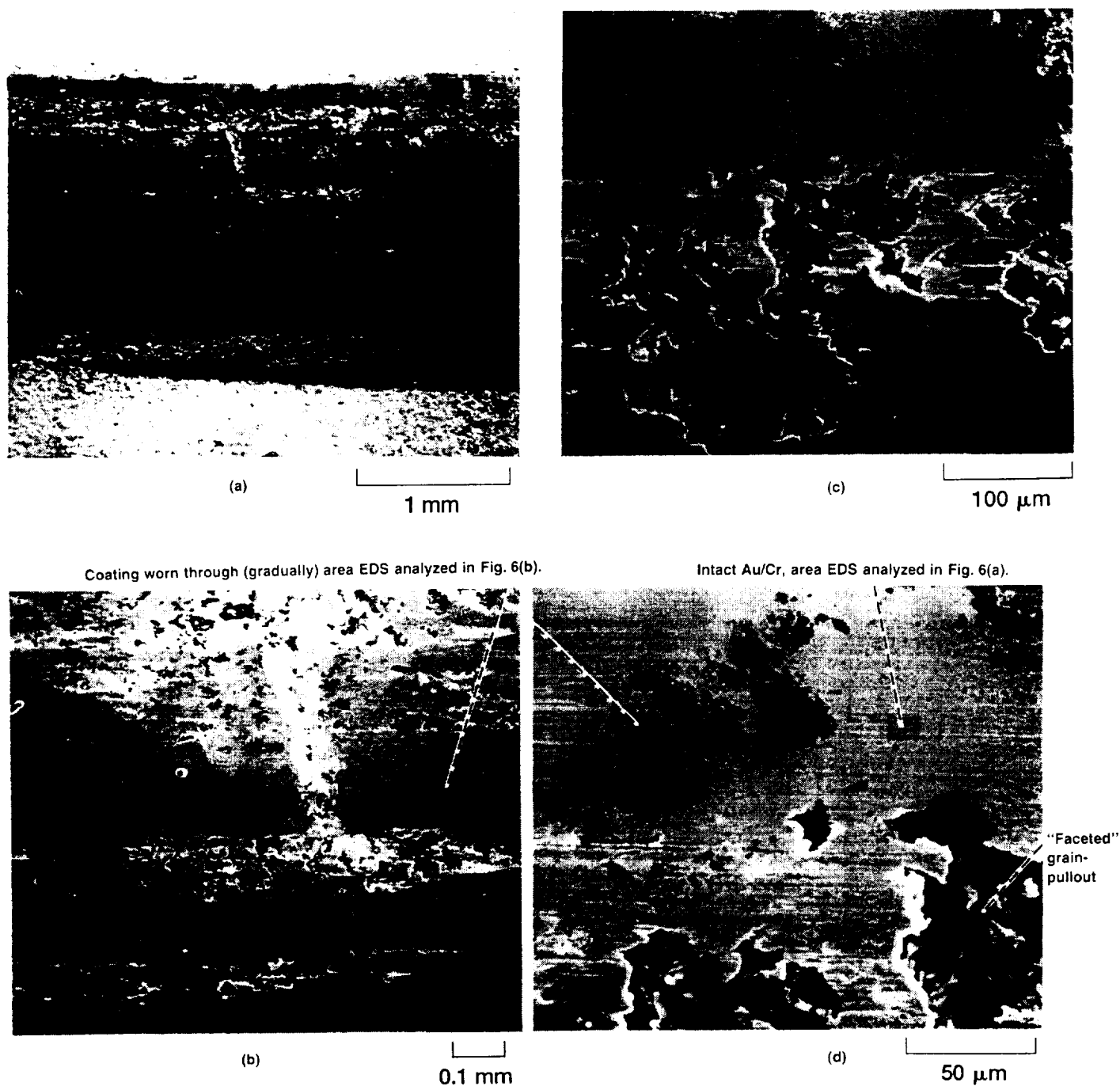


Fig. 5—Electron photomicrographs of Au/Cr wear track at various magnifications. Test conditions: 9.8 N load (1 ms^{-1} sliding velocity, 250°C , air atmosphere).

2. Small localized regions showing gradual thinning out or wearing through of the Au-Cr film.
3. Small-faceted surface regions which appear to be grain pullout of the Al_2O_3 substrate.

EDS analysis, shown in Fig. 6(a) of the predominant region, indicates that the gold lubricating layer is still largely intact. Where this layer has been removed, a faceted Al_2O_3 substrate is revealed, suggesting a grain pullout mechanism. This is shown by call out in Fig. 5(d). In other adjacent areas the coating appeared to be simply wearing through, suggestive of a more gradual wear mechanism, as also shown in Fig. 5(d). The corresponding EDS analysis, given in Fig. 6(b),

shows that these areas are largely depleted of gold but still contain chromium, further suggesting a gradual wear process.

Thus, it appears that even after substantial sliding has taken place, the Au-Cr film continues to provide lubrication, under low load conditions. Furthermore, the wear process is typified by gradual film wear not catastrophic film delamination or failure.

Effect of Velocity

Sliding velocity had a minimal effect on the coefficient of friction, as shown in Table 3. At both 25° and 500°C the friction coefficients obtained at higher velocities were within

TABLE 3—HIGH-SPEED FRICTION COEFFICIENT AND PIN WEAR FACTOR
($\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1} \times 10^{-8}$) DATA SUMMARY
(Test conditions: 4.9 N load, air atmosphere, 30 min test duration)

°C	UNCOATED DISKS		Au/Cr SPUTTER COATED DISKS							
	1 m/s		1 m/s		5 m/s		10 m/s		15 m/s	
	μ	k_{pin}	μ	k_{pin}	μ	k_{pin}	μ	k_{pin}	μ	k_{pin}
25	$0.85 \pm .03$	232 ± 7	$0.49 \pm .06^A$	$7.0 \pm .8^A$	0.46	18.9	0.54	488	0.49	998
500	$0.69 \pm .05$	1400 ± 150	$0.35 \pm .05$	9.5	0.41	891	0.38	756	0.31	123
800	$0.76 \pm .02$	450 ± 50	$0.30 \pm .02$	$2.6 \pm .8$	0.31	637	0.26	1250	0.22	1070

Notes: Values with no error indicated are based on single data points, all others represent multiple (typically six) data points with one standard deviation uncertainty.

^A 60 min test.

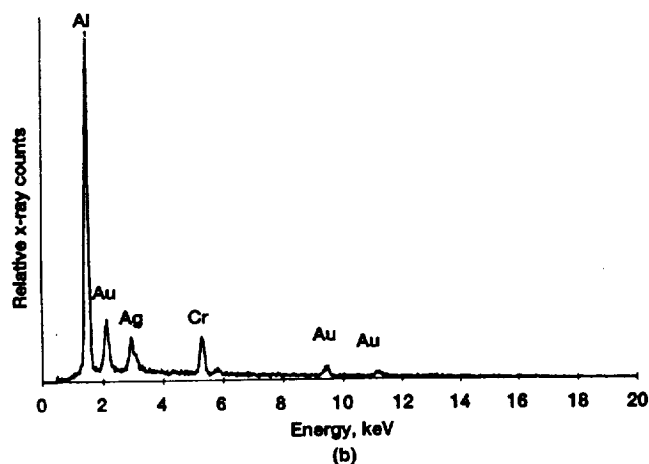
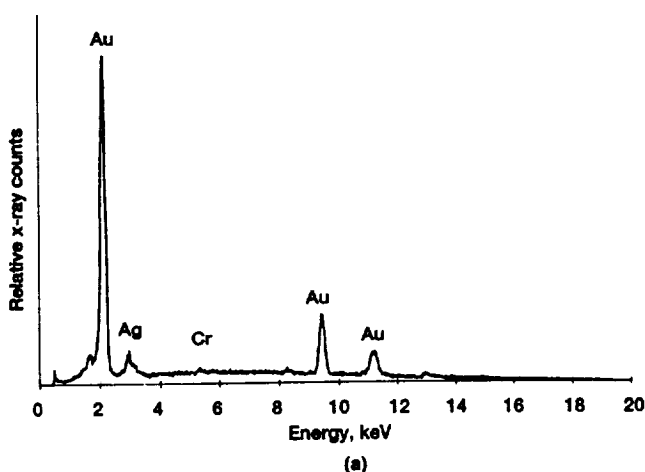


Fig. 6—EDS spectra of Au/Cr wear track corresponding to Fig. 5.
(a) intact Au/Cr coating
(b) wear-through area showing presence of Cr and Al_2O_3 (Al peak) substrate Ag peak from overlay coating used to prepare specimen for EDS analysis, electron beam energy 20 kV

data scatter of those obtained at a nominal velocity of 1 ms^{-1} . At 800°C a slight downward trend in friction coefficient was noted $\mu = 0.30$ at 1 ms^{-1} and 0.26 and 0.22 at 10 and 15 ms^{-1} , respectively. The authors could postulate that this was due to frictional heating and therefore further softening of the gold lubricating layer. However, since the high-speed test results are based on singular datum points, further study may be required to better understand the effects of velocity on tribo-performance.

Coating wear life was significantly reduced at velocities higher than 1 ms^{-1} . Test duration had to be reduced from 60 to 30 minutes to minimize substrate damage. The measured wear lives (in total sliding distance) at velocities in excess of 1 ms^{-1} were substantially lower than those routinely achieved during low-speed sliding. Pin wear factors increased by one to three orders of magnitude during high-speed testing. The increase in wear with sliding velocity is consistent with the results obtained by Bloomberg et al. (14) for dry sliding of alumina, which they attributed to a more severe wear regime dominated by uncontrolled crack propagation. However, they also showed a concurrent increase in friction coefficient which was absent in our study. It appears that although the gold solid lubricant could not prevent wear of either the alumina pin or the substrate at high sliding velocity, friction was still reduced.

CONCLUDING REMARKS

At 800°C extended life was achievable at a load of 4.9 N with a sliding velocity of 1 ms^{-1} even after sliding for nine hours (82 km). It was not possible to definitively quantify coating life in the current study due to the large number of tests and samples that would have been required. Long-term film durability is still under investigation and appears to be controlled, due to the diffusion of Cr, by the initial Cr thickness and operating temperature as well as by load and sliding velocity.

Based on tests to date the service envelope of the Au/Cr solid lubricant can be quantified as follows. The Au/Cr coating reduces friction and wear across the wide temperature range of 25 to 1000°C . Temperature had a dramatic effect on friction. Increasing the temperature from 25° to 1000°C resulted in friction reduction of 50 to 60 percent. No definite trends of wear with temperature were observed. Coating life was significantly reduced and pin wear increased when the load exceeded 19.6 N or the sliding velocity was raised above 1 ms^{-1} .

Even under the most severe sliding conditions, i.e., high load and temperature, the wear mechanism was not catastrophic delamination but rather a localized failure of the protective layer. The Au/Cr film can provide adequate lubrication to moderately loaded, low-speed sliding contacts at temperatures as high as 1000°C .

REFERENCES

- (1) Helms, H. E. and Thrasher, S. R., *Engineering Applications of Ceramic Materials*, ASM, Metals Park, Ohio, pp 25-31, (1985).
- (2) Sutor, P. and Bryzik, W., *Recent Developments in the Adiabatic Engine*, SAE SP-738, SAE, Warrendale, Pennsylvania, pp 37-49, (1988).
- (3) Bowden, F. P. and Tabor, D., *The Friction and Lubrication of Solids*, The Clarendon Press, Oxford, pp 111-119, (1950).
- (4) Hutchings, I. M., *Friction and Wear of Engineering Materials*, CRC Press, pp 30-33, (1992).
- (5) Erck, R. A., Erdemir, A. and Fenske, G. R., "Effect of Film Adhesion on Tribological Properties of Silver-Coated Alumina," *Surf. and Coat. Tech.*, **43-44**, pp 577-587, (1990).
- (6) Erdemir, A., Fenske, G. R., Nichols, F. A. and Erck, R. A., "Solid Lubrication of Ceramic Surfaces by IAD-Silver Coatings for Heat Engine Applications," *Trib. Trans.*, **33**, pp 511-518, (1990).
- (7) Maillat, M., Chattopadhyay, A. K. and Hintermann, H. E., "Preparation of Silver Coatings to Obtain Low Friction in Alternating Sliding at 570°C," *Surf. and Coat. Tech.*, **61**, pp 25-29, (1993).
- (8) DellaCorte, C., Pepper, S. V. and Honey, F. S., "Tribological Properties of Ag/Ti Films on Al₂O₃ Ceramic Substrates," *Surf. and Coat. Tech.*, **52**, pp 31-37, (1992).
- (9) Rairden, J. R., Neugebauer, C. A. and Sigsbee, R. A., "Interdiffusion in Thin Conductor Films—Chromium/Gold, Nickel/Gold and Chromium Silicide/Gold," *Metallurgical Trans.*, **2**, pp. 719-722, (1971).
- (10) Eustathopoulos, N., Chatain, D. and Coudurier, L., "Wetting and Interfacial Chemistry in Liquid-Metal-Ceramic Systems," *Mat. Sci. and Eng.*, **A135**, pp 83-88, (1991).
- (11) Mattox, D. M., "Thin Film Metallization of Oxides in Microelectronics," *Thin Solid Films*, **18**, pp 173-186, (1973).
- (12) Benoy, P. A. and DellaCorte, C., "Tribological Characteristics of Sputtered Au/Cr Films on Alumina Substrates at Elevated Temperatures," *Surf. and Coat. Tech.*, **62**, pp 454-459, (1993).
- (13) Sliney, H. E. and DellaCorte, C., "A New Test Machine for Measuring Friction and Wear in Controlled Atmospheres to 1200°C," *Lubr. Eng.*, **57**, pp 314-319, (1991).
- (14) Bloomberg, A., Olsson, M. and Hogmark, S., "Wear Mechanisms and Tribo Mapping of Al₂O₃ and SiC in Dry Sliding," *Wear*, **171**, pp 77-89, (1994).
- (15) Samsonov, G. V., *Handbook of Physicochemical Properties of the Elements*, IFI/Plenum, New York, (1968), p 243.

Tribological characteristics of sputtered Au/Cr films on alumina substrates at elevated temperatures

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Abstract

This paper describes research to evaluate the tribological properties of alumina pins sliding against thin sputtered gold films on alumina disk substrates. A chromium interlayer 250 Å thick was first deposited on the alumina test disks to enhance the adhesion and high temperature wetting of the gold films. The Au/Cr films were tribotested in pure sliding in a pin-on-disk tribometer under a load of 4.9 N at 1 m s⁻¹. The test atmosphere was room air at temperatures of 25, 500 and 800 °C and the test duration varied from 60 to 540 min.

The use of the Au/Cr films reduced the friction by about a factor of 2 compared with the unlubricated alumina sliding couple. The coatings prevented wear of the alumina substrate disks and reduced the pin wear by one to two orders of magnitude. In addition, wear lives in excess of 200 000 sliding passes (9 h) were observed during sliding at 800 °C. The results suggest that these films show promise for the lubrication of many high temperature sliding components.

1. Introduction

The development of mechanical components and devices that operate at ever-increasing temperatures demands the concurrent development of material-lubricant combinations that can survive such extreme environments. High temperature tribology has been called “the single greatest problem facing the adiabatic engine” where temperatures of 560 °C are expected at top ring reversal [1, 2]. Even higher temperatures, up to 1000 °C, are expected in sliding engine and control surface seals for proposed hypersonic vehicles [3]. Ceramic materials, because of their light weight, high temperature stability and low thermal conductivity, are promising candidates for the above and other applications. However, unlubricated ceramics present unacceptably high friction and wear rates [4, 5].

Solid lubrication, in the form of thin, soft metallic films such as gold or silver, appears to be an effective method for lubricating ceramics [6, 7]. The beneficial value of thin, soft films in lubricating hard substrates has long been documented [8]. Friction is reduced in the contact zone owing to the low shear strength of the soft coating coupled with the high load-carrying capability of the hard substrate [9]. The coatings must of course adhere to the substrate during sliding. Unfortunately,

relatively inert metals such as Ag and Au typically adhere poorly to ceramic substrates [10].

The interfacial bond can be improved by applying the coatings with a high energy technique such as ion-beam-assisted deposition (IBAD) [6, 7, 11]. Bare alumina pins sliding against alumina disks coated with IBAD Au and Ag films reduced friction and wear significantly compared with unlubricated disks in tests run at temperatures up to 400 °C. However, metallic films such as Ag still dewet ceramic substrates at moderate temperatures (about 500 °C) [7, 12].

Sputter deposition of Au and Ag coatings is another, less costly method of application, but debonding and dewetting at high temperature remain a problem. A more adherent sputtered film can be produced by introducing a thin bond layer of a more reactive metal between the inert Au or Ag coating and the ceramic substrate [12]. The “binder” or bond metal reacts with the substrate to form a tenacious interlayer that still presents a metallic surface to the non-reactive solid lubricant. The Au or Ag then wets and adheres to the bond metal. A recent paper by one of the authors shows that alumina disks sputter deposited with Ag and a Ti binder layer do not dewet after being subjected to heat treatment in air at 850 °C as do disks sputtered only with Ag [12]. They also retain their good tribological properties when tested at room temperature after heat treatment. More recent testing by the authors has shown

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that the Ag/Ti composite coating performs well at temperatures up to about 400 °C. At higher temperatures coating delamination occurs, resulting in high friction and wear and excessive transfer to the pin.

Au/Cr is another coating combination that has shown promise in other ceramic applications. As examples, chromium has been used in the electronics industry to bond gold contacts to ceramics and has also been used in the brazing of ceramics [10, 13, 14]. For tribological purposes, gold's low shear strength and excellent thermal and chemical stability make it a potentially good solid lubricant over a wide temperature range. In the Au/Cr system a thin layer of chromium would act as the interfacial bond between the ceramic substrate and the inert gold solid lubricating layer.

In the present paper sputter-deposited Au/Cr coatings on alumina substrates were tested in sliding against bare alumina pins at 25, 500 and 800 °C. Baseline comparative tests were run at the same temperatures with unlubricated alumina disks and also with disks coated only with Au sliding against unlubricated alumina pins. During preliminary testing it was observed that heat treating the Au/Cr-coated disks prior to testing significantly improved the coating adhesion. Therefore a 6 h heat treatment at 725 °C was instituted. Following tribotesting, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analyses were conducted to assess the performance and utility of these coatings.

2. Experimental details

2.1. Materials and coatings

Disks of 99.4% pure alumina with a nominal diameter of 6.35 cm and surface polished to approximately 0.4 μm r.m.s. were used in all tests. The pins, also of 99.4% Al_2O_3 , were cylindrical rods 0.953 cm in diameter with both ends finished to a 2.54 cm radius of curvature. Pin and disk property data and fabrication information can be found in a previous publication [12]. Targets of 99.999% Au and 99.95% Cr were used for sputter deposition of the solid lubricating films.

The pins were cleaned using the following five-step process: rinse with ethyl alcohol, polish with 0.3 μm alumina powder, rinse with tap water, rinse with deionized water and finally blow dry with laboratory air. Prior to sputtering, the disks were ultrasonically cleaned for 15 min each in acetone and then methanol, after which they were dried with nitrogen. The disks were back-sputter etched for 5 min at 0.500 kW and 20 mTorr with ionized argon atoms in a final cleaning process before deposition of the surface coatings.

A 250 Å layer of chromium was sputter deposited on each alumina disk, followed by a 2 μm layer of gold.

These coating thicknesses were chosen on the basis of previous experience with Ag/Ti films as a good "starting point" for this initial research. Sputter times were 25 s at 0.500 kW and 8 mTorr for the chromium and 282 s at 1.00 kW and 8 mTorr for the gold coating. The sputtering times necessary to achieve the desired thicknesses were determined experimentally and verified using surface profilometry on a quartz standard. Figure 1 shows an SEM image of an as-deposited Au/Cr film.

Prior to tribotesting, the disks were annealed in air at 725 °C. Heat treating for 6 h appears, on the basis of initial tribotest results, to form a more tenacious film. Various intermediate times and temperatures were tried before adopting this heat treatment, which may not yet be optimal.

2.2. Apparatus

Pin-on-disk friction and wear tests were carried out in a high temperature tribotester. This equipment has been described fully in a previous publication [15]. Briefly, the pin-and-disk apparatus is enclosed in a resistance-heated furnace capable of attaining and maintaining temperatures of up to 1200 °C. A dead-weight system loads the pin on the disk with a force of 4.9 N. The disks are rotated at 370 rev min^{-1} , resulting in a nominal linear velocity of 1 m s^{-1} . Prior to testing, the disk is carefully aligned to reduce the total indicated run-out to less than 0.025 mm. The friction force and the load force are continuously recorded via a strip chart. In addition, discrete data, including load, friction force, temperature and speed, are sampled and stored every 30 s by a computer acquisition system.

Wear tests were run at temperatures of 25, 500 and 800 °C. Tribotests were initially run for 30 min. The test time was increased to 60 min when it became apparent that the Au/Cr coating was maintaining its integrity for the duration of the shorter tests. Even longer tests, up to 9 h in length, were run to establish the durability of

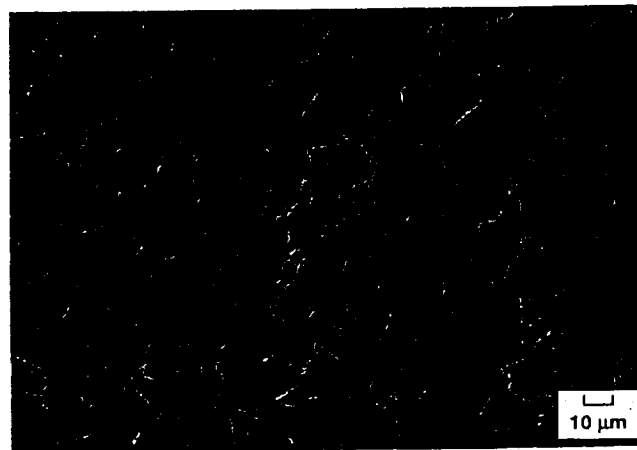


Fig. 1. SEM image of as-deposited Au/Cr coating on Al_2O_3 substrate.

the films. All testing was done in atmospheric air with a relative humidity (RH) of 50%–75% at room temperature.

SEM and EDS were used to image the test specimens and conduct elemental analyses of the disks before and after wear testing. The Al_2O_3 pins were examined only after testing because they had to be coated with a conductive film in order to prevent "charging" in the scanning electron microscope. The pin wear volume was calculated using an optical microscope to measure the wear scar diameter. The disk wear volume was determined using a surface profilometer. Wear factors k ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) were then calculated by dividing the wear volume by the product of the load and sliding distance.

3. Results and discussion

3.1. Tribotesting

3.1.1. Friction

Friction coefficients for the tests conducted, averaged over the first 60 min of testing, are given in Table 1. The friction for the Au/Cr-coated disks was approximately 50%–60% less than on unlubricated disks at all test temperatures. Friction coefficient *vs.* time is plotted for the Au/Cr-coated disks and uncoated alumina disks at each test temperature in Fig. 2. One possible reason why the friction is lower at elevated temperatures is that the shear strength of the gold film is reduced as the temperature is increased, though this reason does not explain why the friction at 500 °C is slightly lower than at 800 °C. However, since the same trends are observed for the unlubricated sliding case, the alumina surface may also have an effect on the friction.

Although several long-term durability tests (up to 9 h or 32.4 km) were run on the Au/Cr disks, only the initial 60 min of testing is shown. The longer tests merely exhibited a continuation of the same frictional behavior. For example, 60 min into one of the long-duration tests at 800 °C the friction coefficient was 0.32, while after 9 h of sliding the friction coefficient had gradually increased

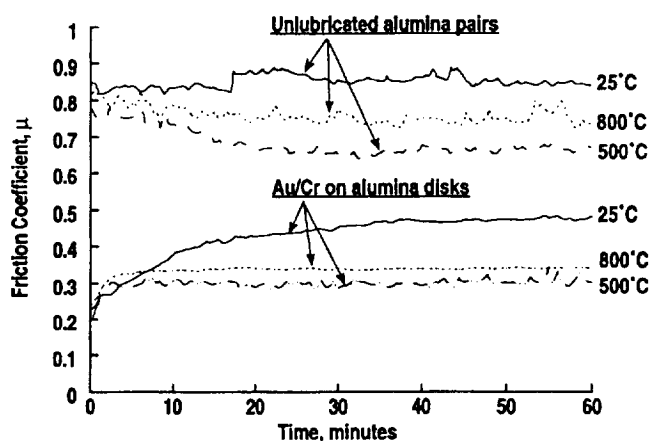


Fig. 2. Friction coefficient *vs.* time for unlubricated and Au/Cr-lubricated alumina specimens (4.9 N load, 1 m s^{-1} sliding velocity, air atmosphere).

to only 0.35. Therefore the additional data points associated with the longer tests were omitted from the plot for clarity.

Because of the preliminary nature of this work and the long (greater than 60 min) life of these films, it is difficult to assign a definite film wear life. Only a limited number of long-term durability tests have been performed. At 800 °C three separate tests ran without failure for 3, 5 and 9 h. Another endurance test at the same temperature failed after approximately 6 h. Coating failure was deduced by rising and fluctuating friction and appears to be a gradual process. At 500 °C coating failure began after 5 h of sliding, while a disk tested at 25 °C continued to perform for 9 h. On the basis of these limited tests under these conditions, the useful coating life is estimated to be between 5 and 10 h of sliding (18–36 km)

3.1.2. Wear

Wear factors for pins tested against uncoated disks and disks sputter coated with Au and Au/Cr films are summarized in Table 1 and plotted in Fig. 3. Pins run on Au/Cr-coated disks exhibited substantially less wear at all temperatures than pins tested on unlubricated

TABLE 1. Friction and wear summary^a. Test conditions: 4.9 N load, 1 m s^{-1} sliding velocity, air atmosphere (40%–60% RH), 60 min test

Disk specimen	Friction coefficient			Pin wear factor k ($10^{-7} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$)		
	25 °C	500 °C	800 °C	25 °C	500 °C	800 °C
Unlubricated	0.85 ± 0.03	0.69 ± 0.05	0.76 ± 0.02	23.2 ± 0.7	140 ± 15	45 ± 5
Au coated	0.24 ± 0.05	^b	^c	1.0 ± 0.2	^b	^d
Au/Cr coated	0.40 ± 0.05	0.30 ± 0.03	0.34 ± 0.02	0.60 ± 0.20	0.16 ± 0.06	1.40 ± 0.40

^aUncertainties represent one standard deviation of the data. At least six repeat tests were run for each data point given.

^bTest not run.

^cFriction was 0.35 until coating delaminated prior to end of 60 min test period.

^dImmeasurable owing to excessive coating transfer from disk to pin.

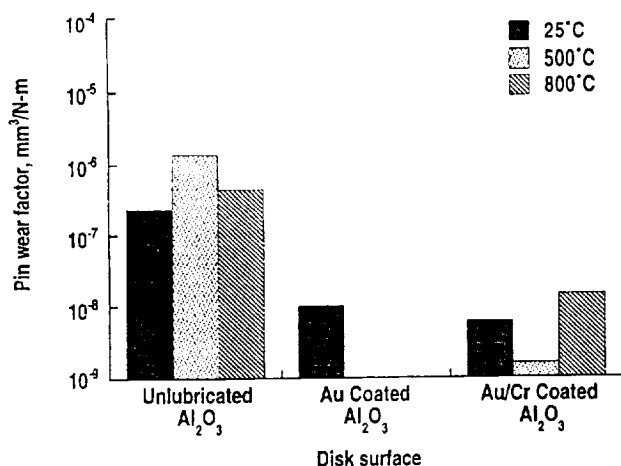


Fig. 3. Pin wear factors k for Al₂O₃ pins sliding against various disk surfaces.

disks. At 800 °C the pin wear is 30 times lower on heat-treated Au/Cr-coated disks than on unlubricated disks.

At room temperature Au films with no Cr interfacial layer also produced substantial reductions in pin wear, approximately 23 times less wear than that of pins tested on uncoated disks. However, when tested at 800 °C, these Au coatings failed by complete delamination in the wear track. Excessive coating transfer from disk to pin precluded accurate and meaningful wear measurements for these tests.

The disk wear for the coated specimens is more difficult to quantify and possibly less meaningful. Post-tribotest surface profilometry indicates that the maximum wear depth is about 2 μm, which corresponds to the thickness of the gold lubricating layer. Thus for the coated disks the wear volume consists primarily of the Au/Cr films. Therefore direct comparison of the lubricated and unlubricated disk wear data cannot be made.

3.2. Surface analysis

SEM and EDS analyses of the wear specimens help elucidate some potential reasons for the long (up to 36 km) high temperature wear lives of the Au/Cr films. Figure 4 shows a photomicrograph of a pin wear scar after sliding for 3 h against an Au/Cr-coated Al₂O₃ disk at 800 °C without failure. A thin transfer film of gold and chromium (as determined by EDS) is observed on the wear surface. Figure 5 shows photomicrographs of the disk wear track from this test. Figure 6 shows the corresponding EDS analysis of the features observed in the wear track. Higher magnifications reveal small (less than 1 μm) rounded patches of gold which have apparently been removed from adjacent larger regions of the coating. These small gold patches are deposited on the chromium layer, which endures even after high temperature testing.

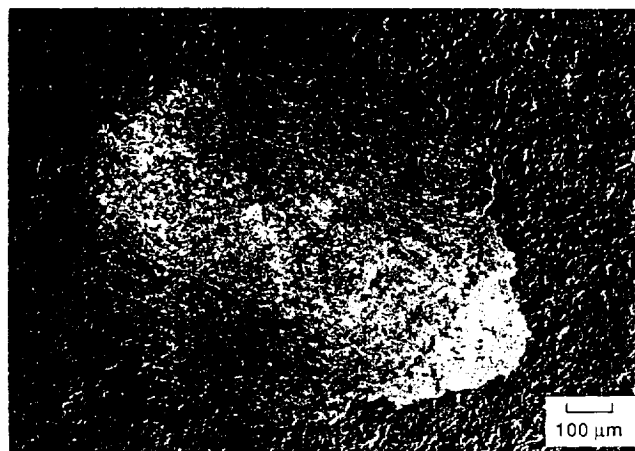


Fig. 4. SEM images of pin wear scar after sliding against Au/Cr film at 800 °C.

No loose debris was observed on or near the disk wear track or pin wear scar, further suggesting that the gold that is removed from the large coating areas is redeposited elsewhere on the wear surfaces and available for continued lubrication. Considering the relatively small thickness of these films, approximately 2 μm, their unexpectedly long wear lives also provide additional support for this type of redeposition lubrication mechanism.

Prior to testing and heating, no chromium is discernible during EDS analysis of the Au/Cr sputter-coated disks. This is to be expected, since the penetration depth of the electron beam is only about 1 μm while the gold layer is 2 μm thick. After annealing for 6 h at 725 °C, a clear chromium peak was observed in the spectra of unworn areas of the disks. These effects suggest that the chromium is diffusing through the gold. Interdiffusion may cause film hardening, analogous to "solid solution strengthening". The existence of this effect is supported by the observation that the Au/Cr films show higher friction at room temperature than the pure gold films. No film hardness measurements were made. EDS examination of alumina pins after sliding against Au/Cr-coated disks also reveals distinct chromium transfer. Although the exact role the chromium plays in film adhesion and wear life is not known, its presence may be enhancing the performance of the gold/alumina sliding contact system.

4. Concluding remarks

The results presented in this paper indicate that the sputtered Au/Cr films effectively lubricate the alumina specimens over a wide temperature range (25–800 °C). Compared with unlubricated alumina sliding couples, both friction and pin wear were substantially reduced at

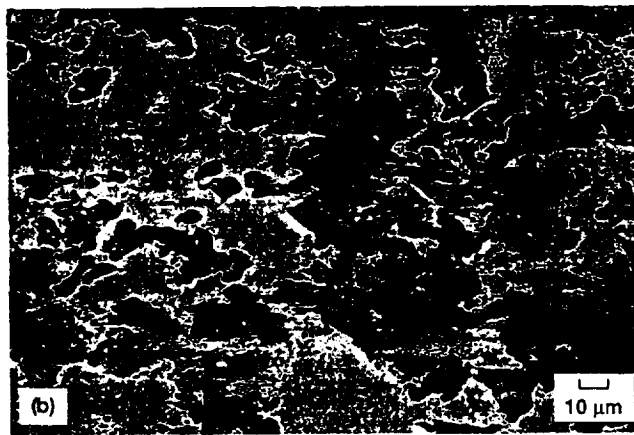
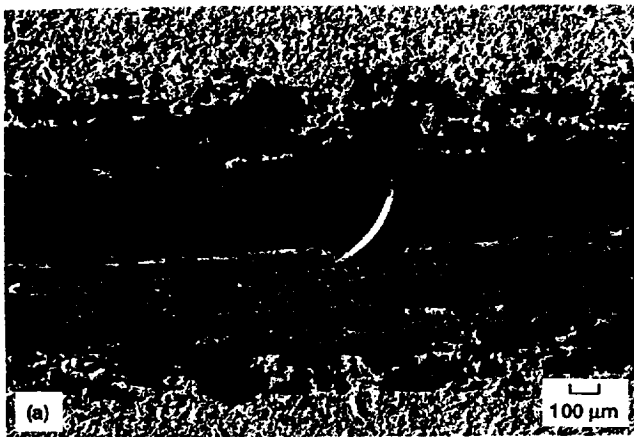


Fig. 5. SEM images of disk wear track of Au/Cr-coated Al_2O_3 specimen after sliding at 800°C. Au (bright regions) appears to migrate from larger regions as small patches. Higher magnification image (c) shows migrating gold patches.

all temperatures tested. Although sputtered gold films without a chromium interfacial bond layer performed adequately at room temperature, coating delamination occurred during sliding at elevated temperatures, suggesting that chromium can enhance the adherence and

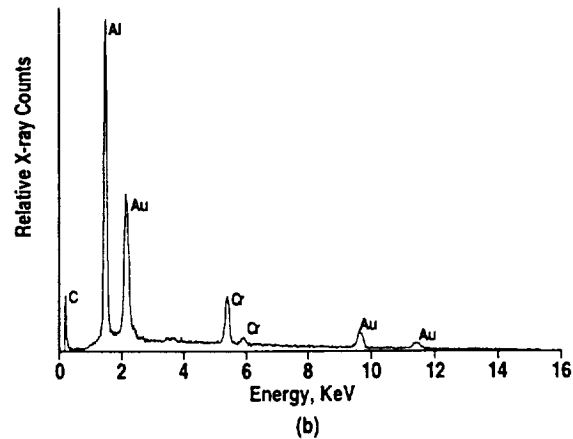
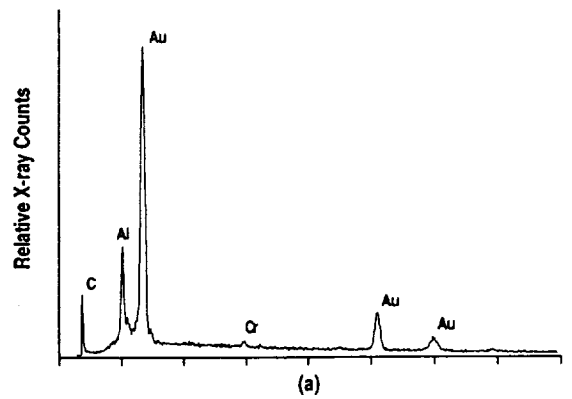


Fig. 6. Corresponding ED X-ray spectra of (a) small gold patch and (b) surrounding darker area showing persistence of Cr layer.

performance of gold lubricant films. On the basis of these results, sputtered Au/Cr films may be appropriate and effective lubricants for advanced high temperature sliding applications.

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References

- 1 R. Kamo, W. Bryzik and P. Glance, *SAE SP-700*, 1987, pp. 1-13.
- 2 P. Sutor and W. Bryzik, *SAE SP-700*, 1987, pp. 165-177.
- 3 B. M. Steinetz, C. DellaCorte and P. Sirocky, On the development of hypersonic engine seals, *NASA TP-2854*, 1988.
- 4 C. S. Yust and J. J. Carignan, Observations on the sliding wear of ceramics, *ASLE Trans.*, 28 (2) (1985) 245-252.

- 5 M. Woydt and K. H. Habig, High temperature tribology of ceramics, *Tribol. Int.*, 22 (1989) 75–88.
- 6 A. Erdemir, G. R. Fenske, R. A. Erck and C. C. Cheng, Ion-assisted deposition of silver films on ceramics for friction and wear control, *Lubr. Eng.*, 46 (1990) 23–30.
- 7 A. Erdemir, G. R. Fenske, F. A. Nichols and R. A. Erck, Solid lubrication of ceramics by IAD-silver coatings for heat engine applications, *STLE Trans.*, 33 (1990) 511–518.
- 8 F.P. Bowden and D. Tabor, *The Friction and Lubrication of Solids, Part 2*, Oxford University Press, Oxford, 1954.
- 9 H. E. Sliney and T. Spalvins, The effect of ion plated silver and sliding friction on tensile stress-induced cracking in aluminum oxide, *NASA TM-105366*, 1992.
- 10 D. M. Mattox, Thin film metallization of oxides in microelectronics, *Thin Solid Films*, 18 (1973) 173–186.
- 11 A. Erdemir, D. E. Busch, R. A. Erck, G. R. Fenske and R. Lee, Ion beam assisted deposition of silver films on zirconia ceramics for improved tribological behavior, *Lubr. Eng.*, 47 (10) (1991) 863–872.
- 12 C. DellaCorte, S. V. Pepper and F. S. Honey, Tribological properties of Ag/Ti films on Al_2O_3 ceramic substrates, *Surf. Coat. Technol.*, 52 (1992) 31–37.
- 13 O. M. Akselsen, Review: diffusion bonding of ceramics, *J. Mater. Sci.*, 27 (1992) 569–579.
- 14 A. J. Moorhead and H. Keating, Joining of ceramics for advanced heavy-duty diesels, *NASA CR-175019*, 1986.
- 15 H. E. Sliney and C. DellaCorte, A new test machine for measuring friction and wear in controlled atmospheres to 1200 °C, *Lubr. Eng.*, 47 (4) (1991) 314–319.